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Two 3D cupric metal–organic frameworks based on the biphenyl-2,3,3′,5′-tetracarboxylate ligand and possessing 1D nanosized channels

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ABSTRACT

From the same starting materials, two novel metal–organic frameworks, namely {(cation)$[Cu_4(bptca)_2(OH)(H_2O)_2]\cdot x(solvent)\}_n$ (**1**) and {(cation)$[Cu_3(bptca)_2(H_2O)_3]\cdot y(solvent)\}_n$ (**2**) (H_4bptca = biphenyl-2,3,3′,5′-tetracarboxylic acid), have been synthesized through the linkage of $Cu_2(COO)_4$ paddle-wheel clusters. The complex **1** possesses both dinuclear $[Cu_2O_2]$ subunits encapsulated into cage-like units and tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ clusters, which exhibits an unusual 3D 4-nodal (4,4,4,8)-connected network with $\{4^{12}.8^{12}.10^4\}\{4^3.8^3\}_4\{4^6\}\{8^6\}$ topology. Reducing the metal-to-ligand ratio, the other 3D (4,4)-connected framework **2** with $\{4^2.8^4\}$ PtS-type topology was constructed under the intervention of mononuclear $Cu(bptca)_2$ and single $Cu_2(COO)_4$ paddle-wheel supporting layers. Notably, both of the frameworks **1** and **2** accommodate infinite open 1D nanosized quadrate channels.

1. Introduction

The engineering of porous coordination polymers, also known as metal–organic frameworks (MOFs), tends to be the most rapidly investigated area not only due to their intriguing architectures but also being potential functional materials probably in diverse areas [1]. Indeed, the pore apertures of MOFs determine the size of the guest molecules, which embodies those functional features as a carrier. In general, the construction of porous structural topologies immensely depends on the organic ligands and the coordination geometry of central metal ions [2]. One successful strategy for making large porous MOFs and avoiding appearance of interpenetration is to construct a framework by the "short axis – long axis" mode [3]. The design solution can maintain a short axis with the long organic links inclined to that axis. The short axis by metal–oxygen bonds is the distance between the long organic links of ligand skeleton along that axis joining the secondary building units (SBUs), and effectively eliminates the possibility of framework interpenetration. Conceptually, the main efforts are centered around the choice of suitable organic multicarboxylate ligands [4]. Among various multicarboxylate ligands, asymmetrical carboxylate ligands have been reported rarely in the fabrication of MOFs [5]. Those can be utilized to form large porous MOFs because of their asymmetrical nature in favor of the short axis – long axis arrangement, in which the organic carbon backbone acts as the longer linkage with the asymmetrical carboxyls leaning against the backbone as the short rods [3]. Meanwhile, the twisted conformations of asymmetrical carboxyl ligands benefit the generation of polynuclear metal clusters for addressing that strategy [6].

Taking these into consideration, we chose biphenyl-2,3,3′,5′-tetracarboxylic acid (H_4bptca) ligand to build MOFs, and the asymmetrical carboxyl-rich ligand may be show miscellaneous coordination modes and build complicated high-connected frameworks due to the rotation of phenyl and carboxylate groups. To the best of our knowledge, only cluster-based $[Tb(Hbptca)(H_2O)_2]\cdot H_2O$, $[Mn_4(bptca)_2(bpy)_2]_n$, $[Cd_4(bptca)_2(DMF)_4]_n$ and several other single-nodal MOFs have been reported up to date [7]. Using the binary Cu(II)/H_4bptca system under the solvothermal conditions, we have prepared two novel MOFs {(cation)$[Cu_4(bptca)_2(OH)(H_2O)_2]\cdot x(solvent)\}_n$ (**1**) and {(cation)$[Cu_3(bptca)_2(H_2O)_3]\cdot y(solvent)\}_n$ (**2**). Interestingly, two MOFs show unusual nanoporous 3D noninterpenetrating frameworks with various polynuclear metal clusters and intriguing topological features, as (4,4,4,8)-connected $\{4^{12}.8^{12}.10^4\}\{4^3.8^3\}_4\{4^6\}\{8^6\}$ topology for **1**, and (4,4)-connected $\{4^2.8^4\}$ PtS-type topology for **2**.

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2. Experimental

2.1. Materials and measurements

All reagents and solvents of analytical grade were purchased from commercial sources and used without further purification. Elemental analyses for C, H and N were recorded on the Elementar model VarioEL III instrument. FTIR spectra were obtained in KBr pellets on a Nicolet Avatar 360 FTIR spectrometer in the 400–4000 cm^{-1} region. The powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku D/Max 3III diffractometer. Thermogravimetric analyses (TGA) were determined with a Netzsch STA449C apparatus under a nitrogen stream using at a heating rate of 10 °C min^{-1}.

2.2. Syntheses of complexes **1** and **2**

Synthesis of $\{(cation)[Cu_4(bptca)_2(OH)(H_2O)_2]\cdot x(solvent)\}_n$ (**1**). A mixture of H_4bptca (0.082 g, 0.25 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol), and two drops of concentrated HNO_3 (63%, aq.) in distilled water (3 mL) and DMA (3 mL) was placed in a 10 mL screw-capped vial, heated to 105 °C for 72 h, and then cooled to room temperature at a rate of 5 °C min^{-1}. The pH value of mother solution is about 6. Blue block crystals of **1** were obtained in 36% yield based on copper. Elemental analyses (%): C, 45.09; H, 2.79; N, 3.94. IR/cm^{-1} (KBr): 3422(s), 3245(m), 2934 (w), 1622(s), 1384(s), 1294(m), 1270(m), 1097(w), 1018(m), 939(w), 772(m), 733(m), 694(m), 664(w), 595(w), 556(w), 487 (m). $\{(cation)[Cu_3(bptca)_2(H_2O)_3]\cdot y(solvent)\}_n$ (**2**) was obtained by the same procedure as that for **1** except that different ratio of the reactant was employed (H_4bptca (0.082 g, 0.25 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.060 g, 0.25 mmol)). Yield: 42% based on copper. Elemental analyses (%): C, 47.35; H, 2.96; N, 4.37. IR/cm^{-1} (KBr): 3426(s), 3253(m), 2804(w), 2483(w), 1610(s), 1429(s), 1369(s), 1028(m), 938(w), 848(w), 777(m), 727(s), 667(m), 596(w), 557 (w), 496(m).

2.3. Crystallographic data collection and refinement

Data were collected at room temperature with a single-crystal Bruker Apex II Image Plate CCD diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å) operating at 50 kV and 30 mA in ω scan mode for **1** and **2**. A multi-scan absorption correction was applied with the use of SADABS. The structures were solved by direct methods using the SIR92 program or SHELXS-97, and then refined with full matrix least-square methods based on F^2 (SHELX-2013) within the WINGX program [8]. Because the guest solvent molecules and free ions are highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules and anion ions, and sets of new diffraction intensities were produced. The large thermal parameters of water are caused by slight disorder. Atoms O10 in **2** are disordered into two positions with site occupancies of 0.5 and 0.5. All hydrogen atoms were generated geometrically except coordinated water molecule, which were located from Fourier maps. Crystal data for two complexes are shown in Table S1. Selected bond lengths and bond angles are listed in Table S2.

3. Results and discussion

3.1. Synthesis

MOFs **1** and **2** are built from almost the same reaction conditions, except for the metal/ligand ratio. The reactant ratio seems to play a key role for the construction of complexes **1** and **2**, because our attempts of the reactant ratio variation under the certain external experimental conditions have led to these complexes rather than any other interesting products formation. The experiments with variation of the reactant ratio also disclosed the critical value of stoichiometric ratios of used precursors on the formation of the complexes **1** and **2**, respectively. The result suggests that the reaction is sensitive to the reactant ratio.

3.2. Description of the crystal structures

Single crystal X-ray diffraction analysis reveals that **1** shows a 3D anionic framework with three kinds of polynuclear clusters and 1D channels occupied by unknown charge-balancing guest solvent molecules. Complex **1** crystallizes in triclinic space group $P\bar{1}$. There are four Cu(II) ions, two $bptca^{4-}$ ligands, one OH^- group and two coordinated water molecules in the asymmetric coordination unit of **1** (Fig. 1a). Presumably, $[(CH_3)_2NH_2]^+$ decomposed from DMA and H_3O^+ might be inclosed into the channels to fit the global charge balance of anionic framework [9]. The guest cations are severely disordered, but whether the confirmation of the guest solvent molecules has little influence on the exploration of main frameworks. Cu1, Cu2 and Cu3 centers are five-coordinated, residing in a distorted square pyramidal geometry. Each Cu1 atom is linked with four oxygen atoms of four carboxylate groups from four $bptca^{4-}$ linkers and one coordinated water molecule (Cu1–O 1.958(6)–2.144(9) Å), Cu2 center is coordinated to four oxygen atoms from four separate $bptca^{4-}$ ligands and one oxygen atom of one hydroxyl (Cu2–O 1.916(5)–2.216(6) Å), while Cu3 is bridged by three carboxylate oxygen atoms of three $bptca^{4-}$ anions and two hydroxyl oxygen atoms (Cu3–O 1.923(6)–2.207(6) Å). Cu4 adopts a distorted octahedral geometry defined by five oxygen atoms of four carboxylate groups from three $bptca^{4-}$ linkers in consideration of a nonnegligible Cu4–O16 interaction of 2.653 Å and one coordinate water ligand (Cu4–O 1.925(6)–2.384(5) Å). For the two independent $bptca^{4-}$ anions in **1**, one exhibits a μ_8-bridging mode with the carboxylate groups in μ_2–η^1:η^1 and μ_2–η^1:η^2 fashions (Scheme 1a). The other tetracarboxylate features a μ_6-bridging mode with μ_2–η^1:η^1 and μ_1–η^1:η^0 fashions of carboxylate groups (Scheme 1b).

Two Cu2 and two Cu3 construct papilionaceous tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ cluster through the bonding of two bridging μ_3-OH and eight carboxylate groups of eight $bptca^{4-}$ ligands (Fig. 1b). It should be noted that the introduction of inorganic anions, such as OH^-, O^{2-} and X^- (X = halogen), plays a very important role in the formation of stable polynuclear clusters [10]. The $[Cu_4(\mu_3\text{-}OH)_2]$ cores are maintained by four different $bptca^{4-}$ ligands to extend into one 1D chain along the opposite directions. The most interesting feature is that four $bptca^{4-}$ anions and two terminal $[Cu_4(\mu_3\text{-}OH)_2]$ SBUs interlink to form a cage-like unit with diameter of 6.6 Å propped up by parallelogram dinuclear $[Cu_2O_2]$ SBU, in which the dimer copper SBUs are constructed by two Cu4 surrounding with six bridging carboxylates of $bptca^{4-}$ from the encircling cage. In the cross side of the wide chain, two Cu1 atoms are bridged by four carboxylates in the bidentate-chelating mode to give a paddle-wheel shaped $Cu_2(COO)_4$ subunit with the Cu–Cu distance of 2.6674(18) Å. Although the metal clusters were well investigated, the clusters-based framework materials with the coexistence of multiple polynuclear cluster SBUs have been seldom documented [11].

Significantly, the assembly of paddle-wheel clusters as rigid SBUs with polytopic carboxylate linkers could generate rigid porous frameworks with permanent porosity and open functionalized metal sites [12]. As a consequence, $Cu_2(COO)_4$ paddle-wheel subunits for different orientations act as square SBUs linking 1D chains